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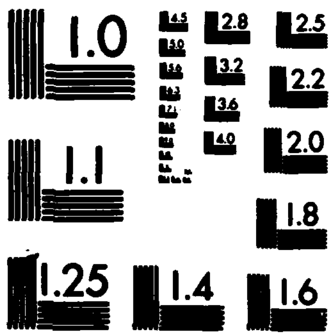

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research was conducted on Epoxy resins, the low temperature relaxation spectra of six epoxy resins was determined via thermally stimulated depolarization measurements. The effect of cross-linking and aging upon physical properties and fracture phenomena has been ascertained for the epoxy resin system diglycidyl ether of butanediol, DGEB and 4-4' diaminodiphenyl sulfone, DDS.

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FINAL REPORT

THE RELATIONSHIP OF ENGINEERING PROPERTIES TO THE MOLECULAR STRUCTURE OF POLYMERIC MATERIALS: DAMAGE ACCUMULATION PROCESSES

by

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February 1984

THE RELATIONSHIP OF ENGINEERING PROPERTIES TO THE MOLECULAR STRUCTURE OF POLYMERIC MATERIALS: DAMAGE ACCUMULATION PROCESSES

FINAL REPORT

The relaxation behavior of several epoxy resin systems which had systematic structural differences were studied via a thermally stimulated depolarization (TSD) technique. Two TSD peaks centered at about 115 K (γ relaxation peak and 185 K (β relaxation peak) were found for epoxy resins cured with a diamine. Structural change, either in the epoxy resin molecule or the amine molecule did not affect these two relaxations. The TSD thermogram of the DGEBA (diglycidyl ether of disphenol A) epoxy resin part only showed a small relaxation at 160 K. This result, together with the fact that post curing increased the β peak height, lead to the conclusions that the β relaxation is most likely due to the newly-created molecular segments during the curing reaction. The relaxation at 160 K was assigned to the epoxy group. This assignment was based upon the fact that the 160 K relaxation of an epoxy homopolymer which had fewer epoxy groups was smaller than that of the parent DGEBA. The activation energy spectra of the β and γ relaxations was studied by the partial heating method and found to be distributed.

An epoxy system consisting of diglycidyl ether of butanediol, DGEB, cured with 4-4' diaminodiphenyl sulfone, DDS, was used in a study of the effect of crosslinking density on the properties of the epoxy resin. Because of the low curing rate at room temperature and the low glass-transition temperature, this system was amenable to a wide range of controlled crosslinking density. The crosslinking density was monitered via FTIR spectroscopy which followed the change in concentration of the epoxy groups during the curing reaction. The bulk density was found to increase linearly with

crosslinking density. The modulus, the upper yield point, the lower yield point and the degree of retraction of a deformed sample all increased with the degree of crosslinking. The β relaxation as measured via TSD was found to vary with crosslinking density, but the γ-relaxation was unchanged. The α-transition was found to decrease in strength but increase in temperature as the crosslinking density increased. It was observed that TSD measurements were a good monitor of crosslinking density of the epoxy resin, particularly during the final stages of the crosslinking reaction.

The effect of sub-Tg aging on the properties of the DGEB cured with DDS epoxy resin system was studied. Aging was found to increase the DSC endothermic peak, the density, and the upper yield point, while the lower yield point was relatively unchanged. These results, together with the observation of the elimination of the DSC endothermic peak by deformation, suggested that the aging effect was eliminated by deformation. The α-transition was found to decrease in strength with aging time. These observations were best rationalized on the basis of the free volume concept.

The fracture toughness of the epoxy resin system DGEB-DDS was studied by varying the crosslinking density and the state of aging. A stable, but rough crack surface, crack propagation was observed with specimens that were 99 percent cured and quenched from 15°C above their Tg to room temperature. When the extent of curing was less than 99 percent or the material was aged for more than 20 minutes at 62°C, crack propagation was of the unstable, stock-slip nature. Aging was found to decrease the fracture initiation toughness dramatically, but the fracture arrest toughness was virtually unchanged. These results were associated with a decrease in the relaxation strength of the α-transition with aging. An increase in crosslinking density was found initially

to reduce the fracture toughness of this epoxy resin, but the fracture roughness increased after about 87 percent curing. The initial decrease in fracture toughness was attributed to a decrease of the relaxation strength of the α-transition, due to room temperature aging, while the increase of the fracture toughness after curing reached 87 percent was explained by the onset of stable-rough crack propagation. Micrographs taken by scanning electron microscopy showed possible existence of blunting during crack propagation and a decrease of blunting with aging.

The correlation between the characteristics of fracture of thin films the epoxy resin system DGEB-DDS with the extent of crosslinking and sub-Tg aging was investigated. Thin-electron beam transparent DGEB-DDS films of varying degrees of cure and aging were strained with a tensile stage in a transmission electron microscope in order to observe the deformation and crack propagation.

As the degree of cure increased from 80 percent to "fully cured," the radius of curvature of the crack tip (as measured from micrographs taken approximately three minutes after straining in the microscope) decreased from 739 nm to 41 nm. A fully cured and room temperature aged DGEB-DDS film had a radius of curvature at the crack tip of 31 nm. There appeared to be a homogeneous deformation zone along the edges of the fracture surfaces, although aging decreased the extent of this deformation. There appeared to be a thin web of inhomogeneously deformed material near a crack tip in a fully cured DGEB-DDS film that had been aged at room temperature. These results were associated with the previously described decrease in main chain molecular mobility observed with increased crosslinking and aging.

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